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"COPOLYMER-LIKE STRUCTURES OF NEMATIC NITROIMINE DIMERS"

BY

L. V. AZAROFF, JACK M. GROMEK, AGYA R. SAINI, AND
ANSELM C. GRIFFIN

LIQUID CRYSTALLINE POLYMER RESEARCH CENTER
UNIVERSITY OF CONNECTICUT
STORRS, CT 06269-3136

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19. A series of nitroimine Siamese-twin dimers joined by an aliphatic chain with n = 2 to 10 were examined by DSC, microscopy, and x-ray diffraction. All dimers except the one having n = 3 undergo transitions to a nematic mesophase without exhibiting distinct relationships. The N-I transitions, in contrast, exhibit a very pronounced alternation with even numbered spacers having much higher clearing temperatures. Magnetically aligned monodomains of the nematic mesophase were examined by x-ray diffraction. In addition to the broad equatorial arcs (yielding interchain separations 1.5 to 5.7Å), up to eight aperiodically spaced meridional reflections were recorded. By positing two possible coupling modes in which either one or both phenyl rings in neighboring dimers overlap, a linear array of coupled nitroimine dimers having two repeating distances along its length is produced. Using such a copolymer-like model, the spacings of the aperiodic meridional reflections and their relative intensities could be reproduced for a random sequence of the two repeat distances and an equal (50:50) probability of single or double overlapped phenyl rings.			
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COPOLYMER-LIKE STRUCTURES OF NEMATIC NITROIMINE DIMERS

by

Leonid V. Azároff, Jack M. Gromek, and Agya R. Saini

Institute of Materials Science

University of Connecticut, Storrs, CT 06269-3136

and

Anselm C. Griffin

Departments of Chemistry and Polymer Science

University of Southern Mississippi, Hattiesburg, MS 39406

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X-ray diffraction diagrams of a homologous series of nitroimine dimers were recorded at their nematic temperatures in a magnetic field of 2,000 G. Two kinds of well aligned monodomains could be distinguished. When the central aliphatic chain contained an even number of methylene groups, the degree of alignment was higher than when n was odd. The aperiodic spacing of up to eight meridional maxima suggested that the dimers form aperiodic linear arrays containing two recurring repeat distances whose lengths were determined by point-model calculations to approximate extended coupled dimers having singly and doubly overlapping phenyl rings, respectively. Line-model calculations based on complete intensity profiles showed that the double overlap was favored when n is even and increases with increasing length of the central spacer chain.

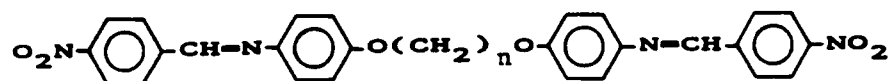
Introduction

In recent years considerable effort has been directed toward the study of the structures of liquid-crystalline polymers and copolymers. Using x-ray diffraction techniques developed for the examination of fibers (1,2), detailed structural information can be obtained provided the polymers are aligned in a strong magnetic field or by mechanical means. As reported more recently (3), quite similar x-ray intensity distributions have been obtained from nematic monodomains of dimer molecules aligned in relatively weak magnetic fields.

The tendency of rod-like (small) molecules to form linear arrays in the nematic state has been recognized for some time (4). Using steric arguments, it can be shown that such packing models can account for the one or two disk-shaped intensity distributions recorded along the meridian in reciprocal space. More recently, nematic alignments have been reported (5) in which neighboring Siamese-twin molecules tended to form linearly extended pairs through dipole-dipole interactions between adjacent dimers with the probability of such pairing increasing as the length of the terminal aliphatic chains increased.

The present investigation was undertaken to verify that such basically liquid systems could organize themselves into structures closely resembling the linear arrays more typical of polymeric fibers. A previously described (3) homologous series of nitroimine dimers consists of two aromatic cores joined by a variable-length

aliphatic spacer and has the general structure



$$n = 2, 4-10$$

Assuming that neighboring pairs of extended dimer molecules can "couple" by means of dipole-dipole interactions as proposed by Chin et al. (5), two coupling modes are most likely in the present case as illustrated in Figure 1. If such couplings join a succession of dimers into an extended array, an aperiodic chain-like structure results as was confirmed by point-model (6) calculations. This previously reported (3) finding is reexamined in the present paper by comparing the continuous intensity distribution function along the meridian in reciprocal space with that calculated from molecular transforms of the proposed chain (line) model. The relative proportion of singly (Figure 1a) and doubly (Figure 1b) overlapped couplings is also established thereby.

Experimental

The synthesis and characterization of the nitroimine dimers has been reported elsewhere (3). Flat-film transmission photographs were recorded for each member of the homologous series for $n=4$ to 10. The samples were heated to about 10°C above their respective melting points in a magnetic field of 2000 G and exposed to a crystal-monochromated beam of Cu K α radiation (7).

The resulting diffraction patterns, typical of aligned nematic monodomains, were converted to digital optical densities using an Optronics microdensitometer operating at 100 micron resolution. The resulting digitized intensity distributions were subsequently manipulated and analyzed using software developed at the Institute of Materials Science for the analysis of x-ray scattering by liquid-crystalline arrays.

In this way, separate meridional intensity profiles were generated for each dimer, corrected for polarization, and plotted in the range of $0 < s (=2\sin\theta/\lambda) \leq 0.3$ in constant s -width steps. These profiles then were available for comparison with calculated intensity distributions. Similarly, azimuthal intensity distributions passing through the equatorial reflections (measured as a function of azimuthal angle from the meridian) were used to determine the Hermans order parameters (8).

Results and Discussion

Probably the most distinguishing property of the homologous dimer series studied is the unusually pronounced alternation in the N-I transition entropies and enthalpies as evidenced by the much higher clearing temperatures when n is even (3). In the present case, this suggests that the degree of ordering in the nematic liquid is considerably greater for the even-numbered spacers. A qualitative indication of this can be judged from the x-ray photographs directly by noting a relative sharpening of all diffraction maxima when n is even. The reciprocal spacings of the observed maxima are listed in Table I by order of appearance

along the meridian in diffraction (reciprocal) space in order to illustrate that they are aperiodic.

TABLE I
Reciprocal spacings of meridional reflections (\AA^{-1})

n	1	2	3	4	5	6	7	8
2	0.051	0.087	0.135	0.189	0.226	0.260	-	-
4	0.048	0.082	0.123	0.163	0.211	0.244	0.278	-
5	0.047	-	0.121	0.162	0.209	0.238	-	-
6	0.045	0.078	0.112	0.149	0.187	0.228	0.258	-
7	0.044	-	0.110	0.149	-	0.226	-	-
8	0.042	-	0.103	0.139	-	0.216	0.241	0.271
9	0.041	-	0.101	0.136	-	0.211	0.235	-
10	0.038	-	0.094	0.129	0.159	0.200	0.227	0.254

In the case of well-ordered crystals, it is possible to deduce their atomic structures by appropriate manipulation of diffraction intensities. In the case of x-ray scattering by liquids, direct use of measured intensities yields, at best, very limited structural information (radial distribution functions). For ordered liquids, however, it is possible to posit structural models and to calculate what their scattering intensities would be so that it is more productive to conduct the comparisons in diffraction space. To this end, it is possible to devise a point model to represent the spatial repetition of the constituent units in the ordered array and to compare its scattering maxima to the observed ones (6,9). More sophisticated analyses (10-12) make use of the complete electron densities (or projections onto the chain axis z), usually by calculating their Patterson

functions $P(z)$ since the scattering intensity function is its Fourier transform.

$$I(s) = T\{P(z)\} \quad (1)$$

If the selfconvolution of the electron density of a molecule (projected onto z) is denoted $M(z)$ and the point-distribution function prescribing how the molecules are repeated along z by $D(z)$, the desired Patterson function is their convolution

$$P(z) = M(z) * D(z) \quad (2)$$

Making use of the properties of Fourier transforms

$$\begin{aligned} I(s) &= T\{M(z) * D(z)\} \\ &= T\{M(z)\} \times T\{D(z)\} \end{aligned} \quad (3)$$

As is well known, if $D(z)$ is a periodic function with period d , then its Fourier transform is a periodic set of delta functions of period $1/d$ and the intensity distribution in reciprocal space consists of discrete maxima also spaced $1/d$ apart. If the distribution function is not periodic but consists of two randomly arrayed periods, then it is necessary to consider all possible combinations and permutations, suitably weighted by their probability of occurrence.

Consider first the distribution function $D(z)$ for a set of point molecules, i.e., their electron densities are projected onto points so that $M(z)$ is a delta function. For the dimer with $n=4$, the most probable repeat distance for point molecules joined by a single overlap (Figure 1a) is $d_1 = 23.9$ A and for double overlap (Figure 1b) $d_2 = 17.5$ A. Assuming that both are equally likely to occur in a chain consisting of ten coupled dimers, the point Patterson has the form shown in Figure 2a. If one assumes further that the two repeat distances may themselves vary by a

few per cent due to thermally induced or other displacements, then the Patterson will be modified as shown in Figures 2b to 2d for (Gaussian) width variations of 0.2 to 1.0 Å, respectively. The diminution of the Patterson peaks with increasing distance from the origin is a characteristic of all aperiodic copolymer systems; the appropriate distribution width being a function of the rigidity and conformational regularity of the constituent monomers.

In the present case of nitroimine dimers, the liquid nature of the system and the relative flexibility of the aliphatic spacers favor a fairly broad distribution width. Thus the liquid crystalline monodomain exhibits discernable (high-probability) translational repetitions only for a fairly small number of aligned molecules so that increasing the actual length of the chain assumed in calculating the distribution function beyond, say, ten molecules has little effect on the resulting distribution function. Three other variables have to be considered, however, the relative fractions of the two kinds of coupled dimers present, their relative orientations, and the resulting relative repeating lengths. A Monte Carlo calculation was used to generate many random chains from which an "averaged" normalized nitroimine chain was determined.

Calculation of a predicted intensity distribution (Equation 3) requires a knowledge of the individual molecular self transforms. Assuming that the dimers favor a fully extended conformation, the self transforms for the even-numbered spacers are shown

in Figure 3. Any deviations from the assumed structures introduce obvious source of error in these calculations, however, as also noted by others (11), small changes in molecular configurations or orientations have negligible effect on the calculated self transforms probably because they are less discernible in their projections on the chain axis.

In the previously reported analysis (3), based on a point-model calculation of the locations of the observed diffraction maxima, a set of optimal repeating lengths was determined for each member of the homologous series. These were used as starting values in the present calculations. Next, the relative ratios of the coupled dimers were varied in steps of 10%, deemed to be the limit of sensitivity of this model. The resulting intensity distributions along the meridian in reciprocal space for $n=6$ are compared in Figure 4 to the observed distribution (bottom of figure) for singly-to-doubly overlapped ratios of 50:50, 30:70, and 10:90, respectively. Since instrumental factors were not incorporated in the calculated intensities, the peaks are too sharp but the peak positions should be unaffected. Similarly, it is not possible to determine a reliable scale factor for relating observed to calculated intensities for a liquid. To facilitate comparisons, therefore, the total integrated intensity for each dimer was considered to be a constant and used to scale the curves in Figure 4. By comparing the positions and the integrated intensities of individual diffraction maxima, it is then possible to select the curve for 30:70 as representing the best agreement with the observed intensity distribution. Table II lists these ratios for all the dimers examined.

TABLE II

Single and double overlap in coupled nitroimine dimers

n	% single	% double
4	40	60
5	70	30
6	30	70
7	60	40
8	20	80
9	50	50
10	10	90

Despite the relatively low reliability of the percentages in Table II (at best, plus or minus 10%), several deductions can be safely made:

1. Double overlap is clearly favored when n is even.
2. Single overlap is favored when n is odd.
3. In all cases, double overlap increases progressively as n increases.

The above results can be understood from steric considerations. For n even, the meso-group vector is parallel to the extended chain vector. Thus for n = 4, a fully extended aliphatic spacer is just long enough to permit double overlaps at both ends of a dimer without steric interferences of the nitro groups. As n (even) increases, such possible steric hindrances rapidly diminish further. For n odd, the meso-group vectors are not parallel to the extended chain vector so that single overlap is sterically easier. As n increases, however, it becomes possible for the aliphatic spacer to distort so that double overlap can be accommodated.

Although the above analysis is based on diffraction data from nematic monodomains aligned in a magnetic field, it is highly probable that the observed tendencies of the dimers to couple persist in the nematic state of unaligned nitroimine dimers as well. It is thus possible to explain the unusually large differences between the clearing temperatures of dimers having odd and even numbered spacers by noting that the stronger interactions formed by double overlap require much higher temperatures to separate them. Similarly, the extreme alternations in the transition entropies are doubtlessly related to the relative proportions of doubly overlapped coupled dimers as is the progressive rise in the transition entropy with increasing n .

The intensity distributions in the equatorial diffraction maxima were used to determine the inter-chain separations by noting the d ($= \lambda / 2 \sin \theta$) values at the opposite half-maximum intensities measured along the equator and the Hermans orientation factor (8) from the azimuthal extent of these maxima. Both sets of values are presented in Table III. The Hermans orientation factor does not appear to change significantly as n increases although the slight drop in the orientation factor as n goes from 8 to 10 may account for the comparable drop in the respective transition entropies from 8.86 to 8.10 J/mole.Kelvin. As expected, the degree of orientation (parallel alignment) is greater for the dimers having even-numbered spacers.

TABLE III
Alignment of dimer chains

n	Inter-chain d (Å)	Orientation factor
4	3.8 ₃ - 5.5 ₉	0.66
5	3.7 ₂ - 5.7 ₅	0.54
6	-- --	0.67
7	3.8 ₈ - 5.6 ₅	0.54
8	3.9 ₇ - 5.4 ₇	0.69
9	3.8 ₃ - 5.6 ₈	0.54
10	3.8 ₅ - 5.4 ₇	0.65

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Figure 1

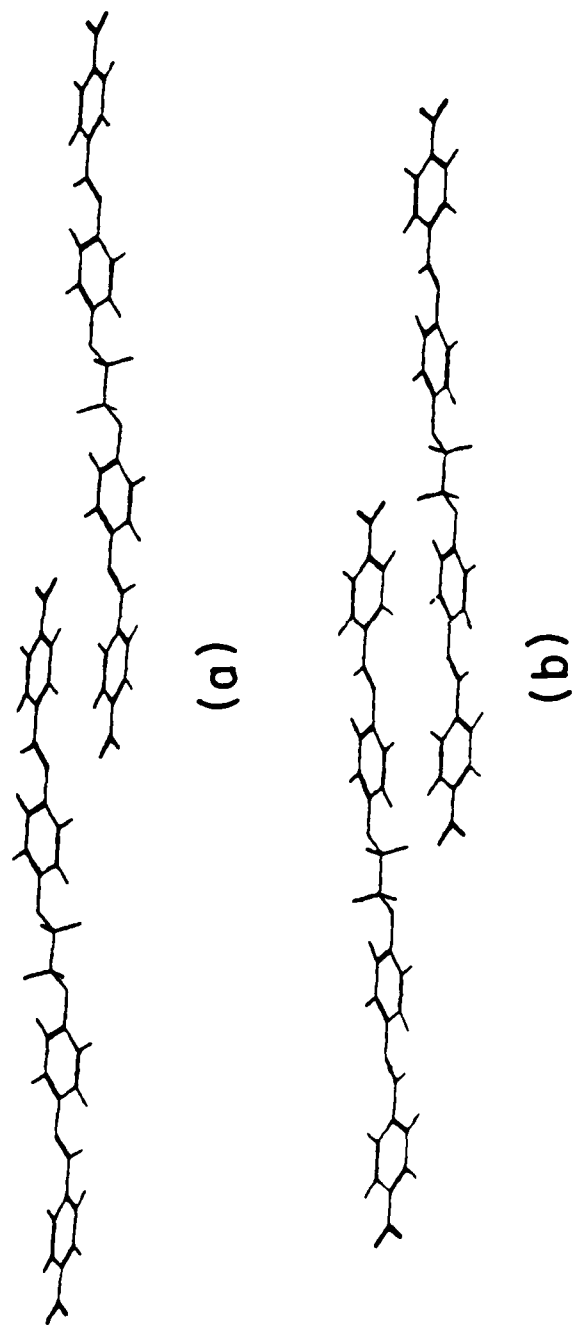


Figure 2

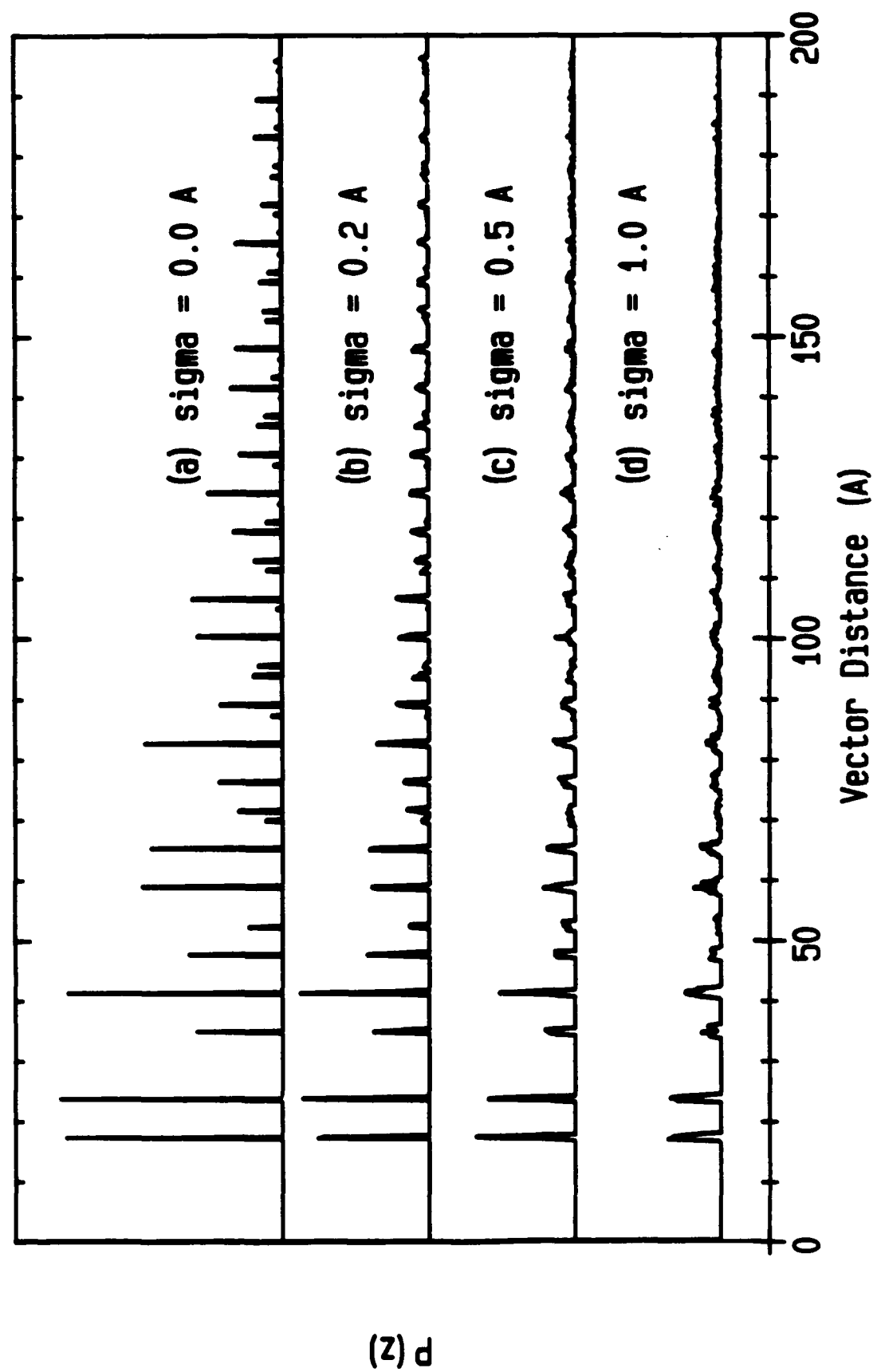


Figure 3

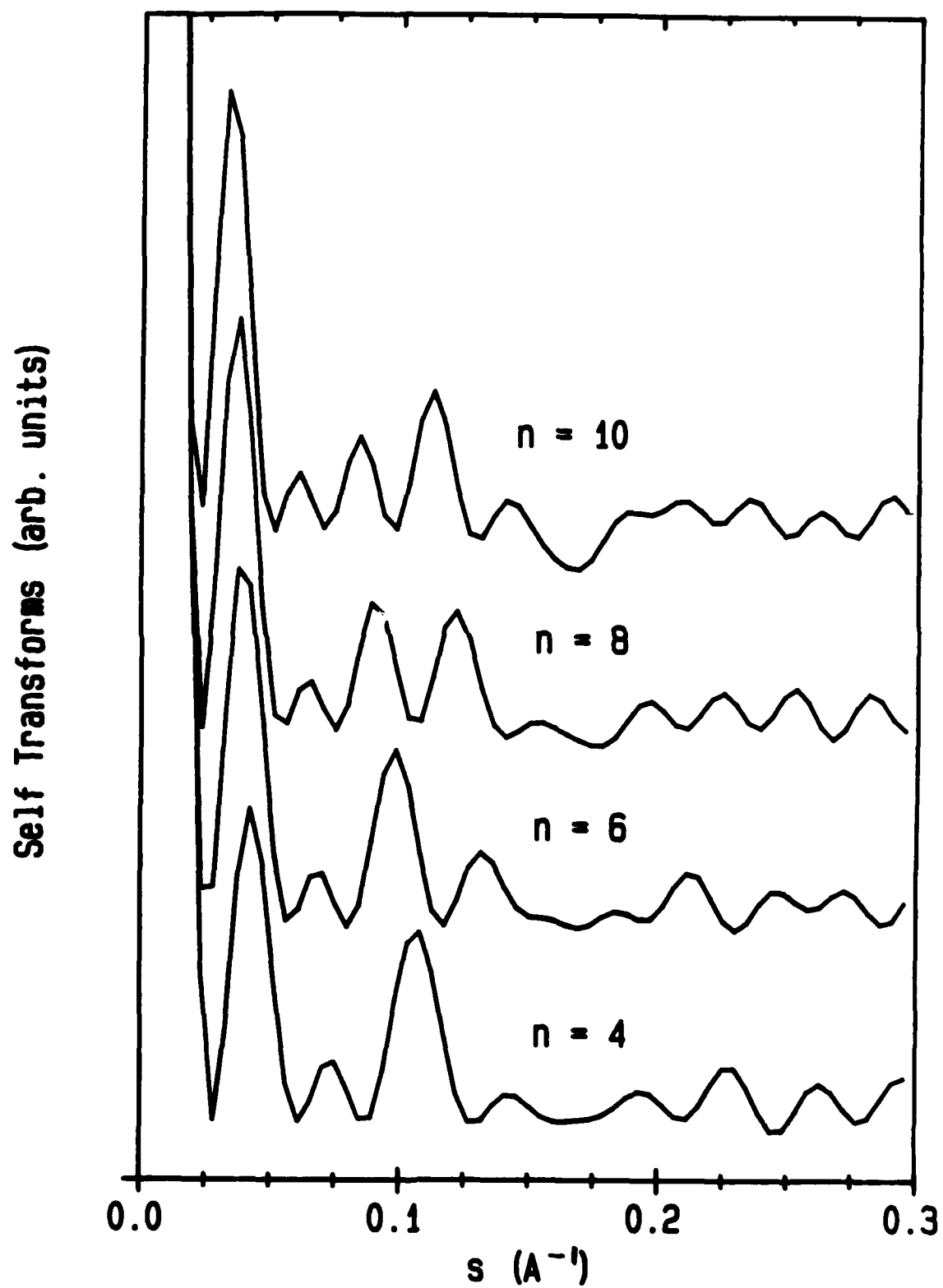
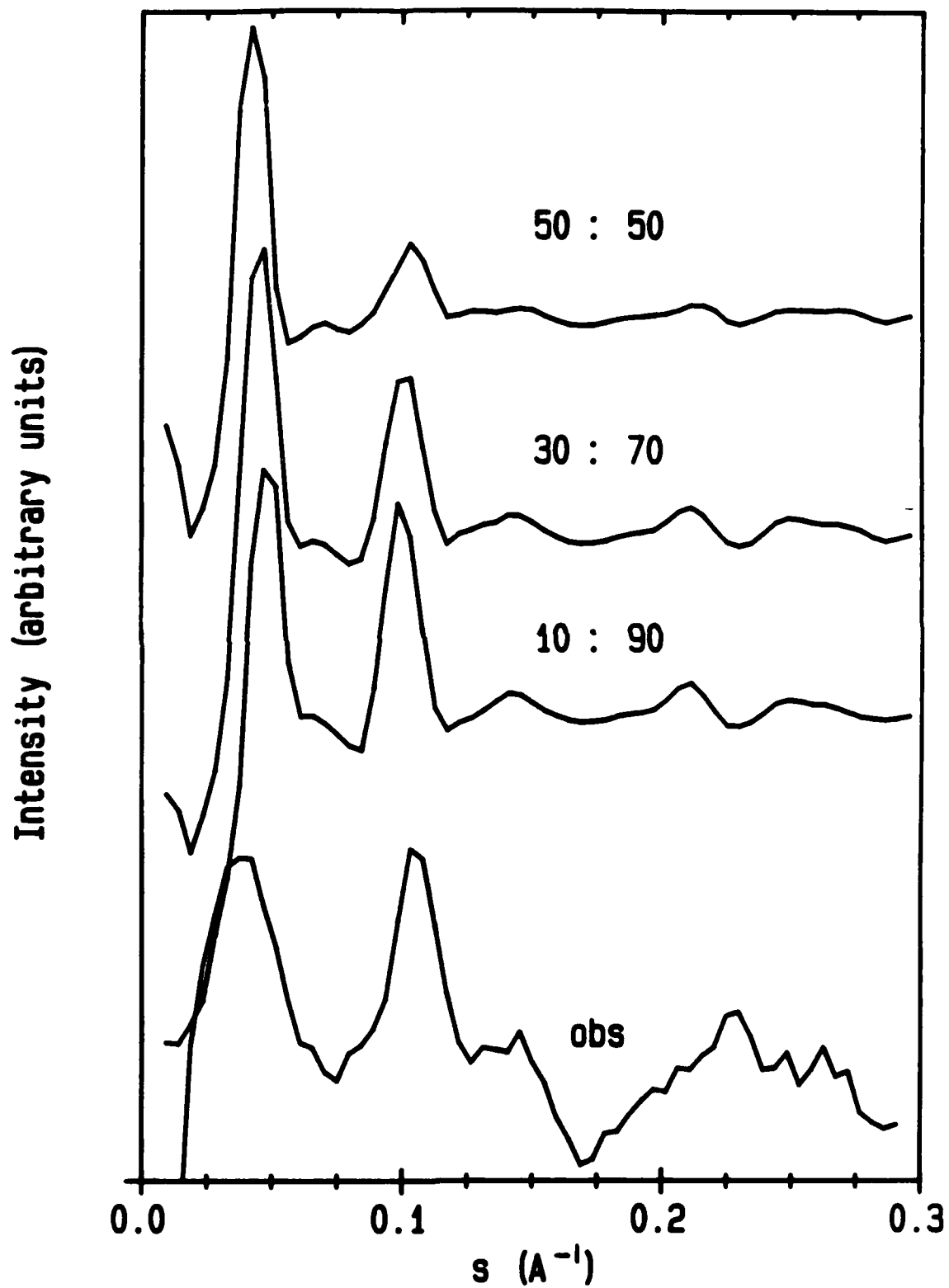


Figure 4



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